Oceanological and Hydrobiological Studies
International Journal of Oceanography and Hydrobiology
Vol. XXXVII, No. 3

Institute of Oceanography | (87-95) | University of Gdańsk
ISSN 1730-413X | 2008 | eISSN 1897-3191

DOI 10.2478/v10009-008-0008-y
Original research paper

Received: *July 05, 2008*
Accepted: *November 07, 2008*

The evaluation of Cr, Ni, Cu, and Co contents in bottom sediments of the Supraśl River and its tributaries

Elżbieta Skorbiłowicz, Mirosław Skorbiłowicz[1]

Institute of Civil Engineering, Technical University of Białystok
ul. Wiejska 45 A, 15-351 Bialystok, Poland

Key words: bottom sediments, heavy metals, rivers.

Abstract

The aim of this study was to evaluate the total and soluble forms of Cr, Ni, Cu, and Co contents in bottom sediments of the Supraśl River and its tributaries. Studies were carried out in August 2005 and March 2006. The total contents of metals were determined, following the digestion of the sediments in nitric acid in a MARS 5 closed microwave system. Soluble forms of metals were extracted with 1 mol dm^{-3} HCl at the ambient temperature. The bottom sediments of the Supraśl and its tributaries are slightly contaminated with chromium. Copper, nickel, and cobalt occur mainly at a geochemical background level. A positive linear correlation between total forms of metal contents and their soluble forms was found.

[1] Corresponding author: *mskorbilowicz@pb.bialystok.pl*

INTRODUCTION

Bottom sediments in water reservoirs are an important part of ecosystems that contribute to element circulation in surface water, and are an indicator of environmental degradation (Kania et al. 2005). The observed increase in heavy metal contents in bottom sediments results from human activities (Helios-Rybicka 1996; Chen et al. 2000; Wardas 2001; Wiśniowska–Kielian, Niemiec, 2005). To a lesser extent, this increase results from natural geological processes. Heavy metals penetrate waters along with industrial and municipal wastes (Angelidis and Aloupi 2000, Baptista Neto et al. 2000, Dauvalter and Rognerud 2001), because of industrial gas and dust emissions (Fang et al. 2004), the combustion of mined fuels in power plants, waste accumulation, and exhaust gas production (Gworek and Kwasowski 2001; Bonar, Zębek 2002; Kaniuczak et al. 2003; Twarowski et al. 2003), and because of surface runoff. Dry and wet atmospheric deposits, fertilizers, and pesticides are the sources of metals in surface runoffs (Salomons and Förstner 1984, Tessier and Hare 1996, Klavins et al. 2000).

The aim of this study was to evaluate the total and soluble forms of Cr, Ni, Cu, and Co contents in bottom sediments from the Supraśl River and its tributaries.

MATERIALS AND METHODS

The Supraśl River (Fig. 1), which is 93.8 km in length and has a catchment area of 1844.4 km^2, is a right tributary of the Narew River. It reaches the Narew at 299.8 RKm. Podzolic and red soils, comprised of light loamy, loamy, and loose sands, dominate in the analyzed area. Peat fills most of wide sections of the upper and lower Supraśl valley. The river is a source of drinking water for the city of Białystok (surface intake); its basin is surrounded by an indirect protective zone. The location of measurement points was designed to make it possible to evaluate the influence and range of the main tributaries of disposed sewage within the basin. Six measurement points were selected on the Supraśl River: in Mościska, Michałowo, Gródek, Supraśl, Nowodworce, and Fasty. The following flows in the Supraśl basin were also investigated: Płoska (in Cieliczanka), Słoja (in Lipowy Most), Czarna (in Wasilków), Biała (in Białystok), and Sokołda (in Sokołda). Single measurement points were selected on each of the above flows near their outlets.

Studies of the Supraśl River and its tributaries were carried out in August 2005 and March 2006. Carvalho et al. (1999) insist that sampling should be done in at least two wet periods to verify results and make them more credible. Collecting a representative sample often constitutes a difficult stage in any

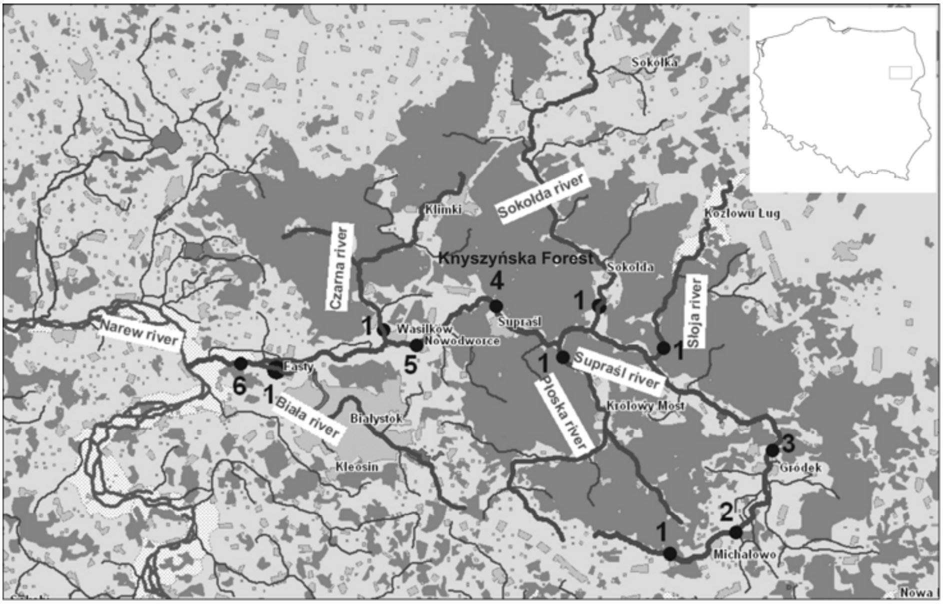

Fig. 1. Location of measurement points.

analytical procedure (Siepak 1997). Bottom sediment was collected in the shore zone where there was an accumulation of suspended material (Bojakowska 2003). A representative sediment sample for each measurement point was achieved by mixing several primary samples taken from various sites at the river edge, at a depth of 0.05 m, and in amounts of not less than 0.5 kg.

Bottom sediment samples were air-dried and sieved through a polyethylene sieve (0.2 mm mesh). That fraction was subjected to analysis, because it is often used in studies connected with geochemical mapping (Thalmann in 1989, Lis Pasieczna 1995). Collecting a representative sample often constitutes a difficult stage in any analytical procedure (Siepak 1997). The total Cr, Ni, Cu, and Co contents were determined after previous digestion in nitric acid (Helios-Rybicka 1986) in a MARS 5 closed microwave system. At the same time, soluble forms of metals were extracted from the sediments using 1 mol dm^{-3} HCl at an ambient temperature. The appropriateness of the methodology was confirmed by means of reference material (NCS DC 73312) analysis. Metal concentrations were determined by means of the AAS technique. Sediment reaction (pH) in water suspension was measured with a potentiometer. Organic matter was analyzed by combustion at 550°C.

Minimum and maximum levels, and arithmetic mean, median, and standard deviations of the tested parameters, were calculated for the bottom sediments studied, separately for 2005 and 2006. Results (two sampling dates made up one result set) were subjected to statistical analysis. A linear correlation between the total contents of tested metals and their soluble forms was found. All calculations were made using Statistica 7.1 software.

RESULTS AND DISCUSSION

Results referring to the contents of the studied metals, and other factors, in bottom sediments from the Supraśl River and its tributaries, are presented in Tables 1 and 2. The composition of bottom sediments varied, which was illustrated by combustion loss differences (0.87-13.80% in 2005, and 0.60-17.96% in 2006) at a median of about 2%. Sediment pH, in most cases, was neutral or weakly alkaline in both years. Organic matter content and the pH of sediments depend on the physicochemical properties of the collected samples, and the performance ways of the soil surrounding studied rivers.

Table 1

Levels of tested parameters in bottom sediments collected in August 2005.

River Localization Statistical data	pH	Organic matter	Content of fraction <0.2 mm	Content											
				Chromium			Nickel			Copper			Cobalt		
				tot	sol	share	tot	sol	share	tot	sol	share	tot	sol	share
		%	% (by weight)	mg kg^{-1}		%	mg kg^{-1}		%	mg kg^{-1}		%	mg kg^{-1}		%
Supraśl Mościska 1	6.50	1.20	9.08	13.4	1.1	8	5.6	0.6	11	1.1	0.7	64	2.6	0.41	16
Supraśl Michałowo 2	6.94	0.70	17.50	14.1	0.9	6	6.2	0.3	5	2.5	1.6	64	2.3	0.3	13
Supraśl Gródek 3	7.33	17.96	13.33	18.7	1.1	6	7.0	0.2	3	1.1	0.5	45	2.3	0.3	13
Supraśl Supraśl 4	6.91	0.60	4.10	13.4	1.8	13	7.3	2.3	32	3.3	2.3	70	3.8	1.31	35
Supraśl Nowodworce 5	7.09	2.11	17.26	11.9	0.8	7	8.5	0.9	11	1.9	0.7	37	3.5	0.86	25
Supraśl Fasty 6	6.19	3.60	15.44	22.7	7.4	33	9.7	2.1	22	6.6	4.3	65	2.8	0.98	35
Sokołda Sokołda	6.80	5.80	7.11	9.7	0.7	7	5.8	0.7	12	1.1	0.8	73	2.4	0.57	24
Czarna Wasilków	7.10	3.90	12.50	7.1	1.1	15	10.9	2.1	19	3.4	1.3	3.8	4.4	1.41	32
Słoja Lipowy Most	7.20	1.21	15.72	4.3	0.5	12	8.1	1.1	14	3.9	1.9	49	4.1	1.32	32
Płoska Cieliczanka	7.10	1.20	9.11	5.5	0.9	16	7.5	1.9	25	2.2	0.9	41	3.3	0.9	27
Biała Białystok	7.50	4.90	1.43	13.5	1.1	8	11.6	2.9	25	4.9	2.9	59	4.1	1.1	27
Arithmetic mean	-	3.90	11.14	12.2	1.6	12	8	1.4	16	2.9	1.6	55	3.2	0.9	25.4
Median	-	2.10	12.50	13.4	1.1	8	7.5	1.1	14	2.5	1.3	59	3.3	0.9	26.8
Standard deviation	-	4.98	5.40	5.47	1.96	8	2.01	0.91	0.09	1.74	1.16	13.21	0.79	0.41	8.17
Minimum	6.19	0.60	1.43	4.3	0.5	6	5.6	0.2	3	1.1	0.5	37	2.3	0.3	13
Maximum	7.50	17.90	17.50	22.7	7.4	33	11.6	2.9	32	6.6	4.3	73	4.4	1.4	35

Remarks: tot – total content, sol – soluble content

Table 2

Levels of tested parameters in bottom sediments collected in March 2006.

River Localization Statistical data	pH	Organic matter	Content of fraction <0.2 mm	Content											
				Chromium			Chromium			Chromium			Chromium		
				tot	sol	share	tot	sol	share	tot	sol	share	tot	sol	share
		%	% (by weight)	mg kg^{-1}		%	mg kg^{-1}		%	mg kg^{-1}		%	mg kg^{-1}		%
Supraśl Mościska 1	7.55	0.87	19.75	7	0.5	7	8.4	1.1	13	0.8	0.1	13	3.9	1.1	34
Supraśl Michałowo 2	7.37	1.56	32.97	8.7	0.8	9	12.4	1.4	11	7.7	5.5	71	4.2	1.2	29
Supraśl Gródek 3	7.30	11.87	12.83	6.5	1.1	17	8.7	1	12	2.1	1.4	67	4.2	0.9	21
Supraśl Supraśl 4	7.32	2.21	19.01	12.3	1.4	12	16.5	3.4	21	12.5	7.5	60	8.9	5.2	58
Supraśl Nowodworce 5	7.21	3.45	19.06	6.1	0.9	16	9.6	1.6	17	6.2	3.3	53	5.1	2.2	43
Supraśl Fasty 6	7.36	1.68	23.43	12.1	1.1	9	10.9	1.9	17	15.2	6.9	45	5.3	1.4	26
Sokołda Sokołda	6.90	5.12	30.12	11.2	2.5	22	8.5	0.9	11	2.6	1.85	71	4.3	1.4	33
Czarna Wasilków	7.40	3.31	2.98	11.9	1.6	14	8.3	2.2	27	9.9	5.2	53	6.1	2.1	34
Słoja Lipowy Most	7.50	2.2	10.35	6.9	0.8	13	8.6	0.8	9	0.8	0.25	31	4.6	1.2	26
Płoska Cieliczanka	7.20	2.2	3.14	7.1	1.1	16	7.3	0.8	11	1.3	0.1	8	3.9	1.3	33
Biała Białystok	6.90	13.80	35.46	15.5	4.5	29	15.8	4.9	31	10.8	5.5	51	5.3	2.1	40
Arithmetic mean	-	4.3	19.00	9.6	1.5	15	10.5	1.8	16	6.4	3.4	48	5.1	1.8	34
Median	-	2.2	19.10	8.7	1.1	14	8.7	1.4	13	6.2	3.3	53	4.6	1.4	34
Standard deviation	-	4.35	11.09	3.15	1.13	6.36	3.14	1.28	7.15	5.19	2.81	21.91	1.44	1.2	1.11
Minimum	6.90	0.87	2.98	6.1	0.5	7	7.3	0.8	9	0.8	0.1	8	3.9	0.9	21
Maximum	7.55	13.8	35.46	15.5	4.5	29	16.5	4.9	31	15.2	7.5	71	8.9	5.2	40

Remarks: tot – total content, sol – soluble content

Metal content was determined in a grain fraction <0.2 mm. In general, the percentage of the studied fraction was not high, namely, in 2005, about 1.43-17.50%, and from 2.98% to 35.46% in 2006, with average values within the range 10-20%.

Statistical analysis of the bottom sediments studied did not reveal any significant correlation between organic matter content and concentrations of total and soluble heavy metals. Similarly, no statistically significant correlation was found between pH and total and soluble contents of the elements studied in the sediments.

The concentration of total chromium in the sediments studied ranged from 4.3 to 22.7 mg kg^{-1}. In comparison to the natural geochemical chromium contents (reaching 5 mg kg^{-1}) reported by Bojakowska and Sokołowska (1998), it can be observed that this element level was exceeded at all but one measurement point. On the other hand, Lis and Pasieczna (1995) find that natural chromium concentration in bottom sediments of unpolluted rivers reaches 10 mg kg^{-1}. Taking this concentration level into account, total chromium level was exceeded at 12 measurement points (about 50%). Sediments from the Supraśl River in Fasty contained the most chromium (22.7 mg kg^{-1} – 2005). Chromium levels in the sediments of the rivers studied were comparable to those in the Dunajec River (Kielian-Wiśniowska 2005), but lower than found in the Wilga River (Wardas et al. 2004). The level of soluble chromium forms ranged from 0.5 to 7.4 mg kg^{-1}. A relatively low soluble form content may indicate low chromium mobility. This is confirmed by the percentage of soluble to total content, which, in the majority of studied samples, was 7-20%. With regard to chromium content in bottom sediments, a statistically significant correlation between total and soluble chromium levels was found ($r = 0.687$, $p<0.05$).

Studies of the bottom sediments revealed that nickel concentration ranged from 5.6 up to 16.5 mg kg^{-1}. Lis and Pasieczna (1995) found the median for nickel amounted to 6 mg kg^{-1} for sediments from Polish surface water. Only two sediment samples showed nickel concentrations lower than 6 mg kg^{-1}. However, it should be noted that even the highest contents recorded were lower than 68 mg kg^{-1}; Turekian and Wedephol (1961) reported a similar level as geochemical background. The percentage of soluble nickel forms in total nickel, in most samples, was within the 10-25% range. Nickel easily forms fairly stable chelate compounds and complex cations and anions. As in the case of the previously discussed elements, a dependence between total and soluble forms was observed ($r = 0.816$, $p<0.05$).

The median for copper in the analyzed bottom sediments was 2.5 mg kg^{-1} (2005) and 6.2 mg kg^{-1} (2006). Bojakowska and Sokołowska (1998) reported natural geochemical copper levels of up to 6 mg kg^{-1}, and this level was not exceeded in the present study. The highest copper content was found in the Supraśl River at Fasty (15.2 mg kg^{-1} – 2006). Determinations of bottom sediments from the Oder River and its tributaries, made in 1997-2000, revealed much higher values of copper contents. These ranged from 15.0 to 1276 mg kg^{-1} (Helios-Rybicka et al. 2001) In the majority of samples collected, the percentage of soluble copper in total copper concentration ranged from 20 to 60%.

Cobalt content in the river bottom sediments was 2.3-8.9 mg kg^{-1}. The geochemical background, according to Turekian and Wedephol (1961), is 19 mg kg^{-1}. Taking this into account, the analyzed samples can be considered to be unpolluted. The level of soluble cobalt forms was relatively low, ranging from 0.3 to 5.2 mg kg^{-1}. Only one sediment sample showed a concentration above 2.2 mg kg^{-1}.

The very high dependence between copper and cobalt contents in their total forms and in the soluble form of these elements was also observed; the correlation coefficients were $r = 0.970$ and $r = 0.941$, respectively, $p<0.05$ for both cases.

The characterization of the contents of the metals studied, using median values in two periods, revealed that the chromium level was lower and the copper level higher in March 2006; the other two elements had similar median values. When there are changing hydrological or hydrochemical conditions, some elements may be re-mobilized (i.e., de-mobilized). Heavy metals may diffuse from deposited material into the water, and again be precipitated or re-sorbed by organic and inorganic solid particles present in rivers. The status of sediment pollution is affected by catchment area conditions and river-bed processes, as well as by the amount and chemical forms of substances that are disposed of in the waters studied.

Heavy metals contents observed in the Supraśl River and its tributaries reflect potential contamination sources. There are water treatment facilities in Michałowo, Gródek, Sokółka, Supraśl, Wasilków, and Białystok. They are unable to remove sufficient quantities of nutrients and other contaminants from sewage. The lack of sewage systems in many villages also contributes to river pollution. Moreover, a well-developed transportation network is a threat because of exhaust gases. Studies of the Supraśl River revealed some slight differentiation of the tested heavy metals contents in particular sections. The exception is the last analyzed river fragment, below the Biała tributary inlet in Fasty. Pollution from Białystok, transported by the Biała River and then the Supraśl River, considerably influences the increase of chromium, copper, and nickel levels in bottom sediments. There are two road and railroad transport routes near the Biała River inlet, and they may also affect metals concentrations. It is noteworthy that the major part of the Biała River catchment area is urbanized; thus water is exposed to continuous waste disposal. Among other factors, there is pollution disposed of through rainfall collectors, points of purified sewage disposal, the water of the Dolistówka and Bażantarka rivers, and other smaller tributaries, as well as pollution from agriculture.

CONCLUSIONS

1. Bottom sediments from the Supraśl River and its tributaries are slightly polluted with chromium. Nickel, copper, and cobalt contents usually occur at geochemical background levels.
2. The highest contents of the tested metals were found in sediments from the Supraśl River at the Fasty measurement point and from the Biała River, which is a receptacle of municipal and industrial sewage from Białystok.

3. It can be assumed that human economic activity and households, along with runoffs, are sources of the chromium, nickel, copper, and cobalt deposited in the bottom sediments of the rivers studied, including the Supraśl River.
4. A positive linear correlation between the total contents of tested metals and their soluble forms was found.

ACKNOWLEDGEMENTS

This study was financed by the Ministry of Education and Science within the framework of Scientific Project No 3 TO9D 112 28, (2005-2007).

REFERENCES

Angelidis, M.O., Aloupi, M., 2000, *Geochemical study of coastal sediments influenced by river-transported pollution: southern Evoikos Gulf, Greece*, Marine Pollut. Bull. 40, 77– 82.

Baptista Neto, J.A., Smith, B.J., McAllister, J.J., 2000, *Heavy metal concentrations in surface sediments in a nearshore environment, Jurujuba Sound, Southeast Brazil,* Environ. Pollut. 109, 1–9.

Bonar A., Zębek E., 2002, *Road and railroad transport as a danger for natural environment*, Ochrona Środowiska, Przegląd nr 4 s. 7-11.

Bojakowska I., Sokołowska G., 1998, *Geochemical quality classes of bottom sediments*, Przeg. Geol. 46, 1: 49-54.

Bojakowska I., 2003, *Geochemical characteristics of sediments from the Narew River and its tributaries.* [W]: Mat. Konf.: Zagospodarowanie zlewni Bugu i Narwi w ramach zrównoważonego rozwoju, Warszawa - Popowo 23-24 May, 137-146.

Carvalho C. E. V., Ovalle A. R. C., Rezende C. E., Molisani M. M., Salomäo M. S. B., Lacerda L.D., 1999, *Seasonal variation of particulate heavy metals in the Lower Paraiba do Sul River, R, J., Brazil*, Environmental Geology 37 (4) April, Springer-Verlag 45-54.

Chen J.S., Wang, F.Y., Li X. D., Song, J.J., 2000, *Geographical variations of trace elements in sediments of the major rivers in eastern China*, Environmental Geology, Springer-Verlag, 39 (12) November, 1334-1340.

Dauvalter, V., Rognerud, S., 2001, *Heavy metal pollution in sediments of the Pasvik River drainage.* Chemosphere 42, 9–18.

Fang, G.C., Chang, C.N., Wu, Y.S., Wang, V., Fu P.C.P., Yang, D.G., Chen, S.C., Chu, C.C., 2000, *The study of fine and coarse particles, and metallic elements for the daytime and night-time in a suburban area of central Taiwan, Taichung,* Chemosphere 41, 639–644.

Förstnera U., 1981, *Umweltchemische Analyse und Bewertung von matallkontaminierten Schlämmen*, Chmiker Zeitung 105, nr 6, 165-175.

Gworek B., Kwasowski W., 2001, *Influence of motorization on an environment.* [W]: Gworek B. i Mocka A. (red.), Obieg pierwiastków w przyrodzie: monografia t. 1, IOŚ, Warszawa s. 39-48.

Helios–Rybicka E., 1986, *A role of silt minerals in binding of heavy metals by bottom sediments in upper Vistula.* Zesz. Nauk. AGH, Geologia, 1050, 32: 1-123.

Helios-Rybicka E., 1996, *Factors describing the mobilisation processes of heavy metals in the dusts, wastes, contaminated soils, and sediments from the area of a smelting industry*, IGCP 405, s.35-36,.

Helios-Rybicka E., Wardas M., Adamiec E., Strzebińska M., 2001, *Evaluation of rivers Odra and Vistula pollution – past and present.* Geologia 27, 659-671,

Kania K., Malina G., Grotenhuis J. T. C., 2005, *Bottom sediments in river Stoła : secondary focus of pollution or protective barrier for surface water?*, Monografie Komitetu Inżynierii Środowiska PAN vol. 33, 1001-1009.

Lis J., Pasieczna A., 1995, *Geochemical atlas of Poland in scale 1:2 500 000,* Państw. Inst. Geol., Warszawa, 72.

Kaniuczak J., Trąba G., Godzisz J., 2003, *Lead and cadmium contents in soils and plants at selected transportation tract of Zamość region,* Zesz. Probl. Post. Nauk Rol. z. 493 cz. I s. 193-199.

Klavins, M, Briede, A., Rodi, V., Kokorite, I., Parele, E., Klavins, I., 2000, *Heavy metals in rivers of Latvia*. Sci. Total Environ. 262, 175–183.

Snape I., Scouller R.C., Stark S. C., Stark J., Riddle M. J., Gore D. B., 2004, *Characterization of the dilute HCl extraction method for the identification of metal contamination in Antarctic marine sediments*. Chemosphere, 57, 491-504

Siepak J., 1997, *Methods of sampling and sample preparation of water, sewage and sediments for physicochemical analysis*, praca zbiorowa, UAM, Poznań, 118

Salomons, W., Forstner, U., 1984, *Metals in the Hydrocycle.* Springer-Verlag, Berlin.

Tessier, A., Hare, H., 1996. *Predicting animal cadmium concentrations in lakes*. Nature 380, 430–432.

Thalmann F, Schermann O., Schroll E., Hausberger G., 1989, *Geochemischer Atlas der Republik Österreich 1:1 000 000*. Geologische Bundesanstalt, Wien,

Turekian K. K., Wedephol K. H., 1961, Distribution of the elements in some major units of the earth ́s crust. Bull. Geol. Soc. America, 72: 175-184.

Twarowski R., Błachuta J., Liana E., Kaczmarski S., 2003, *Deposition of heavy metals with atmospheric fall.* [W]: Janosz-Rajczyk M. (red.), Mikrozanieczyszczenia w środowisku człowieka. Konferencje 51, Wyd. Politechniki Częstochowskiej, Częstochowa s. 527-538.

Wardas M., 2001, *Research on heavy metals in bottom sediments in southern Poland,* Sympozjum Naukowe Komitetu Chemii Analitycznej PAN Komicja Analizy Wody, Materiały pokonferencyjne pod redakcją J. Siepaka, s. 63-74.

Wardas M., Łojan E., Kuboś E., 2004, *Changes of area management in river Wilga valley near Cracow and their influence on aqueous environment.* Geologia t (30) 214- 231.

Wiśniowska –Kielian B., Niemiec M., 2005, *Heavy metals contents in sediments of selected tributaries of river Dunajec ,* J. Elementom, 10 (2): 435-443.